Characterization and Degradation of Cementitious Materials at Fort Sumter National Monument

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Introduction

Fort Sumter is a Third System fortification built on a sand bar in the Charleston, SC, harbor with construction beginning in 1829. Like other Third System forts, it was designed to withstand a naval threat for a period of a few weeks until reinforcements were hurriedly brought by land to needed locations. The masonry construction was used as a barrier against the smooth bore cannon fire used in warfare in the era of design and construction of the Fort.

The Fort's construction began with careful placement of large granite blocks forming a peripheral foundation on the sand bar. After infill of the area encircled by the granite blocks with shells and sand, wall construction began in 1841 using the masonry materials and design principles dictated by General Joseph Gilbert Totten, Chief Engineer of the United States Army[1]. Reviews of these principles are described in the historic cement literature[2].

Plans for the Fort required about 7.5 million locally made clay bricks. The sources of the bricks were thought to be the Wando River production sites described by Wayne[3]. Wayne points out that the Sea Islands north of the Charleston peninsula had insufficient fresh water for the cultivation of rice, and bricks were produced as a "cash crop". Other bricks were produced along the Cooper River near Daniel Island, also a documented production site of burnt oyster lime. The bricks were floated by barge to construction sites around the Charleston peninsula. Prior to this research, there was only limited knowledge of the sources of the bricks or mortar materials at the Fort.

General Totten's representatives purchased "Lawrence's Rosendale Cement" for the bedding mortar[4]. Totten's mortar recipes were typically one part of cement to two parts of sand by volume. Acknowledging that the cement was a costly component when delivered at distant sites from New York, Totten states, "It appears that when cement mortars are not

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[1] Dr. Russell Horres, *The Building of Fort Sumter*, Presented at The Charleston Museum, May 24, 2011.
[2] *Essays on Hydraulic Lime and Common Mortar and on Lime Burning, Translated from the French with Sect. V.-- BRIEF OBSERVATIONS ON COMMON MORTARS, HYDRAULIC MORTARS, AND CONCRETES, WITH SOME EXPERIMENTS MADE THEREWITH AT FORT ADAMS, NEWPORT HARBOUR, R. I. FROM 1825 TO 1838*, J. G. Totten, Lt. Col. of Eng. and Brevet Co. United States, ASTM STP 1494, Natural Cement, Mike P. Edison Editor (2007).
[3] Lucy B. Wayne, *Burning Brick and Making a Large Fortune at it Too: Landscape Archaeology and Low Country Brickmaking*, Carolina's Historical Landscapes, pp. 97-111, University of Tennessee Press (1997).
[4] Fort Sumter Letter Book, pages 35 and following, citation of November 5th of 1857, Charleston (SC) Museum.

required to be the strongest that can be made – a little lime may be added without great loss of tenacity, and, of course, with a saving of expense"[5]. For Fort Warren, Totten allowed the use of a cement-lime-sand mortar of respective volumetric proportions 2:1:6.

In work for the National Park Service, Walsh examined two mortar specimens from Fort Sumter[6]. In one specimen from the exterior scarp wall, the mortar contained Portland cement "of an early twentieth century vintage" implying that the masonry construction in the area of the specimen was from a relatively modern repair. In the other specimen, the mortar was identified as containing natural cement and non-hydraulic lime, with a cement to lime volume ratio estimated by petrography as "between 1:2 and 1:0.5". Walsh identified the sand in the mortar as containing "medium-grained siliceous natural sand" with a binder (fine mixture of cement and lime) to sand volumetric ratio of 1:2.

Walsh's findings reflect the successive periods of deconstruction (by bombardment) and hurried reconstruction during warfare in the period 1861-5. Further, the Fort was repaired using contemporary materials as its mission changed in 1890 when it was rearmed to protect against international threats. In this paper, specimens were carefully selected from masonry construction thought to have been original to the Fort prior to 1861.

Techniques

Microscopy has been applied to the analysis of the deterioration of clay bricks[7]. Millogo, et. al., used microscopy, thermal analysis and determination of physical properties in the evaluation of adobe bricks[8]. Brosnan and Sanders have used similar techniques with fired clay bricks[9].

The techniques used in mortar analysis are well-known. Elsen published a review paper on the microscopy of historic mortars[10]. Krotzer and Walsh describe acid digestion techniques, instrumental analysis and imaging techniques using polarized light microscopy[11]. The acid digestion techniques are described in ASTM C1324-05, "Standard Test Method for Examination and Analysis of Hardened Masonry Mortar". Chiari has used thermal analysis, a technique identifying weight changes and heat flow within materials during heating, to analyze historic

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[5] ASTM STP 1494, p. 147 (In Reference 2).

[6] *Mortar Analysis Report*, John J. Walsh, Senior Petrographer, Testwell Inc., April 1, 2008.

[7] J. Larbi, *Microscopy applied to the diagnosis of the deterioration of brick masonry*, Construction and Building Materials 18 (2004) 299-307.

[8] Y. Millogo, M. Hajjaji, and R. Ouedrago, *Microstructure and physical properties of lime-clay adobe bricks*, Construction and Building Materials, 22 (2008) 2386-2392.

[9] D. Brosnan and J. Sanders, *Characterization of Clay Bricks and Its Use in Forensic Analysis*, ZI Annual 2012 (in press).

[10] J. Elsen, *Microscopy of Historic Mortars – A Review*, Cement and Concrete Research 36 (2006) 1416-1424.

[11] Dorothy E. Krotzer and John J. Walsh, *Analyzing Mortars and Stuccos at the College of Charleston: A Comprehensive Approach*, APT Bulletin (2009) 40(1) 41-48.

mortars[12]. Brosnan, Sanders and Hart have used combined techniques including chemical and mineralogical analysis, petrography, and thermal analysis to arrive at mortar compositions[13].

One purpose of this paper is presenting the results of the characterization and forensic studies. Another is providing a clear explanation of techniques used in these studies to persons vitally interested in historic preservation who may not be familiar with the instrumental methods.

Characterizing Natural Cement

Cementitious materials are typically characterized by their chemical analysis or "assay" using constituents identified as metal oxide species per the convention employed by cement chemists. The analyses of Rosendale natural cement are shown in Table 1. It is clear that oxides of calcium, magnesium, aluminum, silicon, and iron are the major constituents of the cement. Walsh and Uracius point out that the Rosendale Cement is manufactured by burning/heating of argillaceous ("clay containing") limestone[14].

Table 1: Chemical Analysis of Rosendale Cement

Species	Historic Reference A[15]	Historic Reference B[16]	Modern Rosendale[17]	Contemporary Rosendale (This paper)	Insoluble Residue Contemporary Rosendale
CaO	27.8	33-60	32.3	13.7-28.2	1.1
MgO		12-21	17.6	0.4-3.2	0.3
Al_2O_3	5.5	5.5-10	5.0	4.8-7.9	8.3
SiO_2	27.8	27-33	31.3	51.2-69.4	84.0
Fe_2O_3	4.3		2.4	0.3-1.8	1.5
TiO_2			0.3	0.1-0.2	0.2
Na_2O			0.5	0-1.0	1.6
K_2O			2.0	0.3-2.4	2.9

[12] G. Chiari, G. Torraca, and M. Santarelli, *Recommendatians far Systematic Instrumental Analysis of Ancient Mortars: The Italian Experience*, Standards for Preservation and Rehabilitation, ASTM STP 1258 (1996) 275-284.

[13] D. Brosnan, J. Sanders, and S. Hart, *Application af Thermal Analysis in Preservatian and Restoratian af Histaric Masonry Materials; Part A Characterizatian af Materials*, Journal of Thermal Analysis and Calorimetry (2011) 106 (1) 109-115.

[14] John Walsh and K. Uracius, *Explaring American Natural Cement Rack fram its Natianal Distributian to its Chemistry and Micrastructure*, Presented at the 1st American Natural Cement Conference (2005).

[15] A. Rogers and J. Alexander, Industrial Chemistry, 3rd Edition, p. 304 (1920).

[16] W. Wahl, *On the Compasition af Ancient Cements and Rasendale Cements*, Journal of the Franklin Institute (1873) 204-209.

[17] R. Vyskocilova, W. Schwarz, D. Mucha, D. Hughes, R. Kozlowski, and J. Weber, *Hydratian Processes in Pastes af Raman and American Natural Cements*, ASTM STP 1494 (2008).

The historic references typically provide a less detailed view of constituents than those of modern analyses, as some constituents were typically "grouped together" due to early analysis techniques and reported as a single species (as, for example, combining of Al_2O_3 and Fe_2O_3). Nevertheless, it is obvious that the chemistry of natural cement is variable – a fact well known at the beginning of the 20th century[18]. This chemical variation is partly due to selective mining of cement rock using early techniques of visual rock classification.

Natural cement was burned or "calcined" in periodic and continuous kilns so that it would "set", i.e. exhibit hydraulic activity, when ground and mixed with water. Mineral identification techniques including X-ray diffraction show that contemporary Rosendale cement contains major constituent minerals of anorthite – a calcium alumino-silicate (38.2%), quartz (28.7%), and microcline – a potassium alumino-silicate (12.6%). The familiar compounds in Portland cement are also present including alite - tricalcium silicate (6.4%) and belite - dicalcium silicate (4.0%).

These constituent minerals imply that a "set condition" (hardening) is attained after mixing cement with water through early carbonation of some compounds plus formation of calcium silicate phases. In simple terms, natural cements harden through chemical processes that are largely different compared to hardening of contemporary Portland cement; however, there are likely some analogous setting mechanisms between natural cement and Portland cement.

The thermal analysis of ground natural cement is shown in Figure 1. This Figure contains several results on the same graph making a careful inspection necessary. For example, the green colored line is the weight change on heating (the "TG" axis) providing the percentage of the original weight left at any point in the heating process. The red line provides a measure of carbon dioxide evolution on heating, while the blue and black lines provide information on energy flows and water vapor evolutions respectively.

[18] F. H. Doremus, *The Passing of Natural Rock Cement*, American Architect, p. 99 (1903).

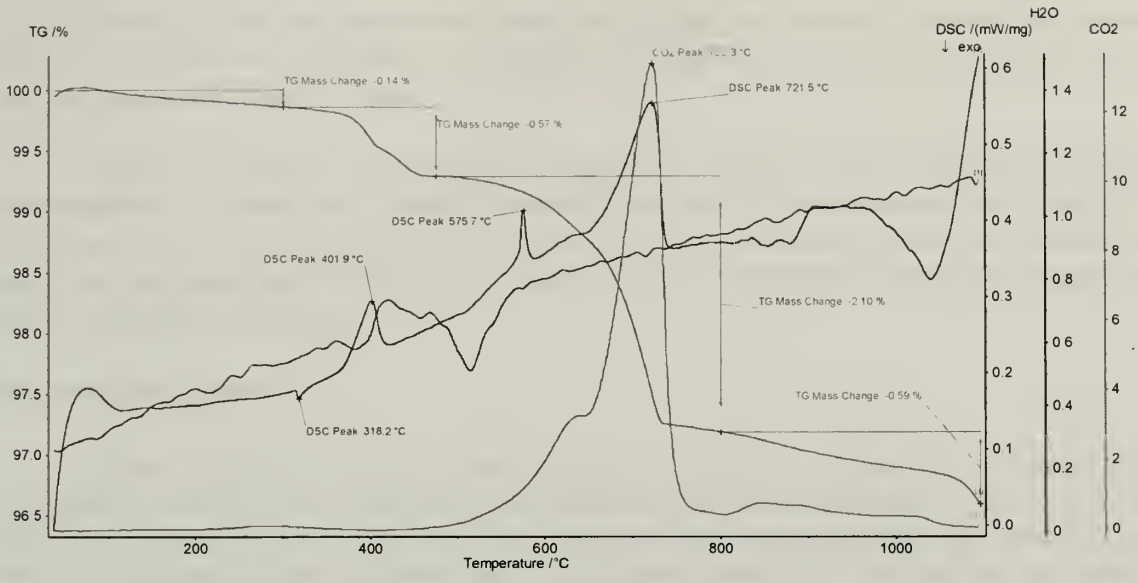


Figure 1: Thermal Analysis of Contemporary Rosendale Cement

The thermal analysis provides the following very important information:

1. Low temperature cement dehydration occurs below 500°C implying that the as-ground cement exhibits a content of phases normally expected in set cement after use, i.e. there has been some formation of compounds during the cement in manufacture (as in grinding) and during storage prior to use. These phases may include carbonates and sulfates of the cement constituents.

2. The cement exhibits an endothermic/heat absorbing reaction at 575°C reflecting the presence of quartz "sand" in the cement rock (See also the insoluble residue analysis in Table 1).

3. The cement exhibits a major decomposition of calcium carbonate at 722°C verifying that the cement was burned to an intermediate temperature between the decomposition temperature of magnesium carbonate, a constituent of dolomitic limestone in cement rock, and that of calcium carbonate also present in the cement rock.

The fact that there is partial decomposition of the cement rock in manufacturing American natural cement strongly suggests that the setting characteristics of the cement are influenced by its thermal history. This is perhaps another reason for the consideration of historic natural cement as a product of notable variation.

The natural cement was additionally characterized by its release of soluble materials when placed in water suspension at room temperature (typically for 20 hours). The cement released about 15,000 parts per million (ppm) or 1.5% (by unit weight of cement) of calcium ions. The solution of potassium was particularly significant at 1357 ppm reflecting the argillaceous nature of the limestone.

Another notable release of soluble material was sulfate at about 5000 ppm, and the decomposition of sulfates may explain the weight loss in the cement below 500°C (Figure 1). The release of soluble metals such as calcium and potassium provide credence to the idea that the initial set/hardening of the cement, in part, is due to atmospheric carbonation processes and the formation of sulfates.

Mortars at Fort Sumter

Mortar analysis included determination of physical properties, chemical and mineralogical analysis, and microscopic examinations. Five mortar specimens were examined with three of the specimens obtained from positions above the mean high tide level and two from below ground or mean high tide level. The physical properties of the mortars are shown in Table 2. All measurements were made using mercury intrusion porosimetry (MIP) because of the small size of the specimens. In MIP, mercury is forced into the pores of the specimen under pressure allowing for a calculation of the amount of porosity (apparent porosity) and for a calculation of the pore sizes present in the specimen.

Table 2: Physical Properties of Mortar Specimens

Specimen	5 - Bedding Mortar Above Sea Level	6 - Pointing Mortar Above Sea Level	11 - Bedding Mortar Above Sea Level	3 - Bedding Mortar Below Sea Level	15 - Barracks Remains Below Ground Level
Location	**Left Flank**	**Sally Port**	**Right Flank**	**Left Flank**	**Interior**
Bulk density, g/cm^3	1.32	1.23	1.62	1.73	1.81
Apparent porosity, %	44.1	43.1	31.6	24.3	22.7
Fraction of porosity <1 micron diameter	29.4	6.5	23.5	74.7	83.1

It is interesting that the submerged mortars constantly exposed to sea or ground salts exhibit near normal porosity values, but they exhibit a significantly larger fraction of "fine" pores, i.e. those less than one micron in diameter. By contrast, the mortars above mean high tide level exhibit seeming high apparent porosities, but they also exhibit near normal fractions of fine pores. The data suggests that there is an ion uptake from sea or ground

salts resulting in low porosities in specimens with constant salt contact. At the same time, salt water corrosion results in very high fractions of fine pores in submerged specimens.

The chemical analyses and other data for the mortar specimens are shown in Table 3. For specimens not exposed to sea water, the magnesium oxide (MgO) content is a first suggestion that the mortars contained natural cement. Two of the mortars (Nos. 5 and 3) exhibited very low calcium oxide (CaO) suggesting extreme solution of calcium from the mortar in sea water.

Table 3: Chemical Analyses and Other Data for Fort Sumter Mortars

Specimen	5 - Bedding Mortar Above Sea Level	6 - Pointing Mortar Above Sea Level	11 - Bedding Mortar Above Sea Level	3 - Bedding Mortar Below Sea Level	15 - Barracks Remains Below Ground level
Location	**Left Flank**	**Sally Port**	**Right Flank**	**Left Flank**	**Interior**
CaO	0.59	37.22	11.22	0.59	22.25
MgO	7.44	10.59	4.61	0.57	9.63
Al_2O_3	0.98	1.94	0.88	1.39	1.66
SiO_2	66.85	15.08	73.26	70.22	47.95
Fe_2O_3	3.49	1.32	1.15	4.06	1.52
TiO_2	1.01	0.10	<0.02	1.33	0.05
Na_2O	<0.5	0.70	<0.5	<0.5	<0.5
K_2O	0.57	1.25	0.13	1.34	<0.05
Insoluble Residue, %	60.74	16.20	76.48	65.21	48.15
XRD Mineralogy	Calcite, quartz, sodalite	Calcite, quartz	Calcite, quartz, sylvite	Calcite, quartz, iowaite, bassanite, brucite	Calcite, quartz, epiodite
Soluble Sodium or Na (ppm of solids)	839	2092	149	2066	851
Soluble Calcium or Ca (ppm of solids)	3752	513	918	1807	3184
Soluble Chloride or Cl (ppm of solids)	1232	2706	148	5801	7406
Soluble Sulfate or SO_4 (ppm of solids)	7218	1555	509	824	350
Rough Mix Proportions by Volume Cement:lime:sand	1:2:4	1:2½:¼	1:4:9	ND	1:3.5:3

All of the mortars exhibited water soluble species at room temperature. The mortars with low residual CaO content (Nos. 3 and 5) exhibit high soluble sodium content (Mortar 15 was exposed to ground salts, and the solution was exacerbated by salt water infiltration). Most mortars exhibited new mineral salts formed during service by salt water exposure (sodalite, sylvite, iowaite, bassanite, and epiodite). Lubelli linked chloride and sulfate in salt water to the solution of calcium from the mortars[19]. This provides a likely reason for reduced CaO in some of the mortars at Fort Sumter.

Petrographic analysis using polarized light microscopy confirmed the presence of Rosendale cement in the historic mortars. A typical photomicrograph is shown in Figure 2 where a Rosendale cement relic (CR) is shown in the field with a lime relic (LR) and porosity (P) in a carbonate matrix. Scanning electron microscopy with energy dispersive X-ray analysis confirmed the phase identifications.

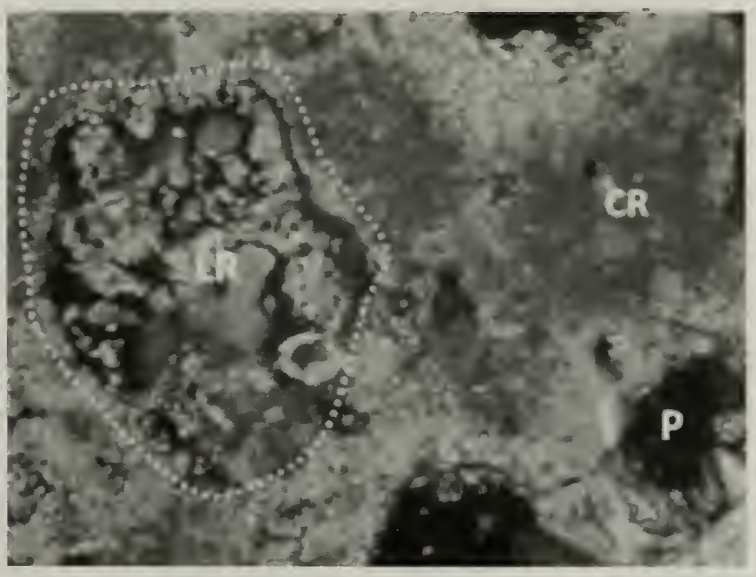
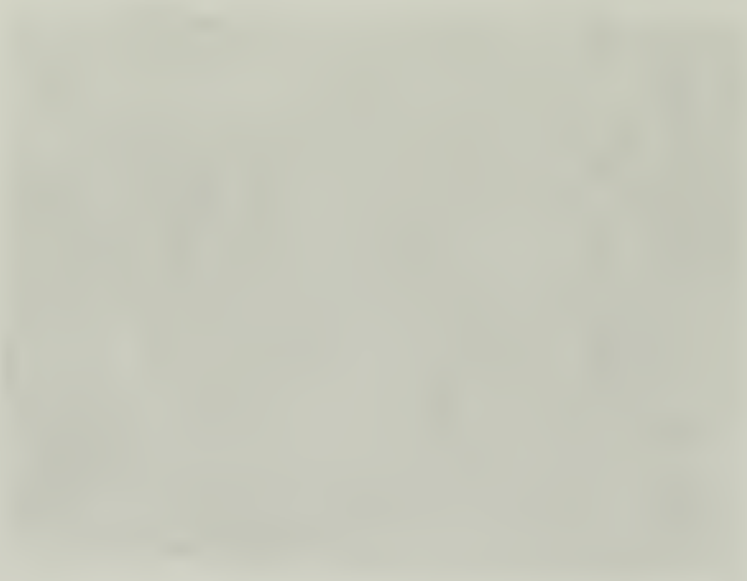


Figure 2: Typical Mortar Photomicrograph (ca. 150X)

The rough mix proportions of the mortars (Table 3) at least are conceptually similar to the Totten formula of one part of fine material (cement and lime) to two parts of sand. All of the bedding mortars exhibit a greater volumetric proportion of sand to fines. It is apparent that the masons at Fort Sumter during construction mixed to a certain consistency that they liked rather than following an exact prescribed recipe.

One very interesting finding was salt scaling on the exterior walls of the Fort where there had been pointing repairs with ordinary Portland cement mortar (Figure 3). This is a classic case of "brick scaling" caused by excessive solution of calcium from the repair mortar

[19] B. Lubelli, R. van Hees, and C. Groot, *The role of sea salts in the occurrence of different damage mechanisms and decay patterns in brick masonry*, Construction and Building Materials 18 (2004) 119-124.



in the presence of sea salts. Such scaling is technically known as cryptofluorescence, and the scaling is due to subsurface expansions within the bricks via salt crystallization. Thus, cryptofluorescence is a damaging mechanism to the historic materials, while surface discolorations known as efflorescence are a non-damaging cosmetic defect in masonry.

Figure 3: Salt Scaling On the Lower Fort Walls Pointed with Portland Cement Mortar

A cryptofluorescence failure on the Fort is shown together with scanning electron microscope photomicrographs in Figure 4. On this face of the Fort, the Portland cement pointing mortar used in modern repairs has completely worn away revealing the "pink" colored Rosendale cement-based bedding mortar. The effect of the calcium solution from repair mortar and infiltration into the bricks with moisture is evident in the "cupped shape" of the residual brick. The scanning electron microscope investigation identified the mineral phase ettringite near the periphery of the brick. It is well-known that the formation on ettringite results in expansive forces. This expansion resulted in damage to the historic bricks as shown in the photograph.

Cubic salts in center (Ca Present)

Ettringite near edge in brick. (calcium sulfoaluminate)

Figure 4: Cryptofluorescence Failures on Fort Sumter

Conclusions

Masonry mortars used at the Fort Sumter National Monument contained Rosendale natural cement and lime generally following the directives of General Joseph Totten, Chief Engineer of the United States Army when the Fort was designed and when masonry construction began in 1841. The analytical results in this study indicate that sea salts have attacked the original masonry mortars dissolving calcium from the mortars. There are indications of an ion exchange between the salt water and the mortars. Portland cement based mortars used in 20th century repairs have contributed soluble calcium to the brickwork causing "scaling damage" known as cryptoflorescence. The significance of these results, in part, is a caution to those involved in restoration of historic masonry to consider the calcium solution by environmental agents so as to do no harm to the historic structures.

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